Supporting information for

The Nanoscale Carbon *p-n* Junction between Carbon Nanotube and N, B-Codoped Holey Graphene Enhances the Catalytic Activity towards Selective Oxidation

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Materials and Characterization:

Dicyandiamide (Sigma-Aldrich, 99%), monohydrate glucose (Sigma-Aldrich, >99.5%), boric acid (Sigma-Aldrich, >99.5%) were used as received without further purifications. Multi-wall carbon nanotube (Sigma-Aldrich) was used with further purified. To eliminate impurities such as graphite nanoparticles, the raw CNTs were washed with 20% hydrofluoric acid for 5 h and 22% nitric acid for a period of 10 h and then subsequently washed with distilled water until the pH of the CNTs approached 7. The washed CNTs were treated with boiled concentric nitric acid for a period of 0.5 h, and the CNTs were washed with distilled water and acetone.

Morphology analysis was performed on a scanning electron microscope (SEM, JEOL 6700F) at an accelerating voltage of 5 kV. More detailed structural examinations were carried out by transmission electron microscopy (TEM, JEOL 2010F) and high resolution TEM with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out by a Kratos Axis Ultra DLD multitechnique surface analysis system. Zeta potentials of the colloids were measured by Malvern Zetasizer Nano ZS90 (Malvern instruments Ltd., UK) according to the Smoluchowski equation. The photoluminescence spectra were obtained on a Shimadzu spectrofluorophotometer RF-5301PC with a Xe lamp as the excitation light source.

Fabrication of carbon/FTO electrode for Mott−Schottky measurement: 50 mg of carbon sample was mixed with 0.1 mL of terpineol and ultrasonic dispersion for about 1 h. The suspension was dip-coated onto the fluorine-doped tin oxide (FTO) glass substrate. A doctor blading technique was employed to ensure the same thickness for each electrode. The electrode was then dried on a hot plate at 80 °C, and then heated in a quartz tubular furnace in nitrogen at 250 °C for 2 h. A silver wire was then connected to the FTO substrate with the silver colloid paste. Finally epoxy was solidified to cover the FTO substrate, the silver paste and wire to avoid short current in the measurement. Electrochemistry was carried out using a typical three-electrode cell made of quartz, in which the nanocomposite film on FTO, a platinum wire, and a Ag^+/AgCl were employed as working, counter, and reference electrodes, respectively. The supporting electrolyte was 1 M NaOH aqueous.

Synthesis of N, B codoped hoely graphene[1]:

Dicyandiamide (40 g), monohydrate glucose (1 g), and boric acid (0.4 g), deionized water (200 mL) were charged into beaker and heated to 80°C under stirring to remove water. The resulting white powder was transferred into a crucible, heated at a rate of 2.4 °C min^{-1} to 600 °C, and stayed at 600 °C for 2 h under a flow of nitrogen. The material was then heated further at a rate of 2.4 °C min^{-1} to 1000 °C and maintained at that temperature for 1 h. The sample was then allowed to cool naturally to room temperature under the protection of N_2.

Preparation of NBG/CNTs nanocomposites:

NBG/CNTs (10:1): NBG (10 mg), CNTs (1 mg), 40 mL deionized water were added in a vial. The mixture was sonicated for 2 hours; **NBG/CNTs (5:1):** NBG (5 mg), CNTs (1 mg), 40 mL deionized water were added in a vial. The mixture was sonicated for 2 hours; **NBG/CNTs (1:1):** NBG (1 mg), CNTs (1 mg), 40 mL deionized water were added in a vial. The mixture was sonicated for 2 hours.

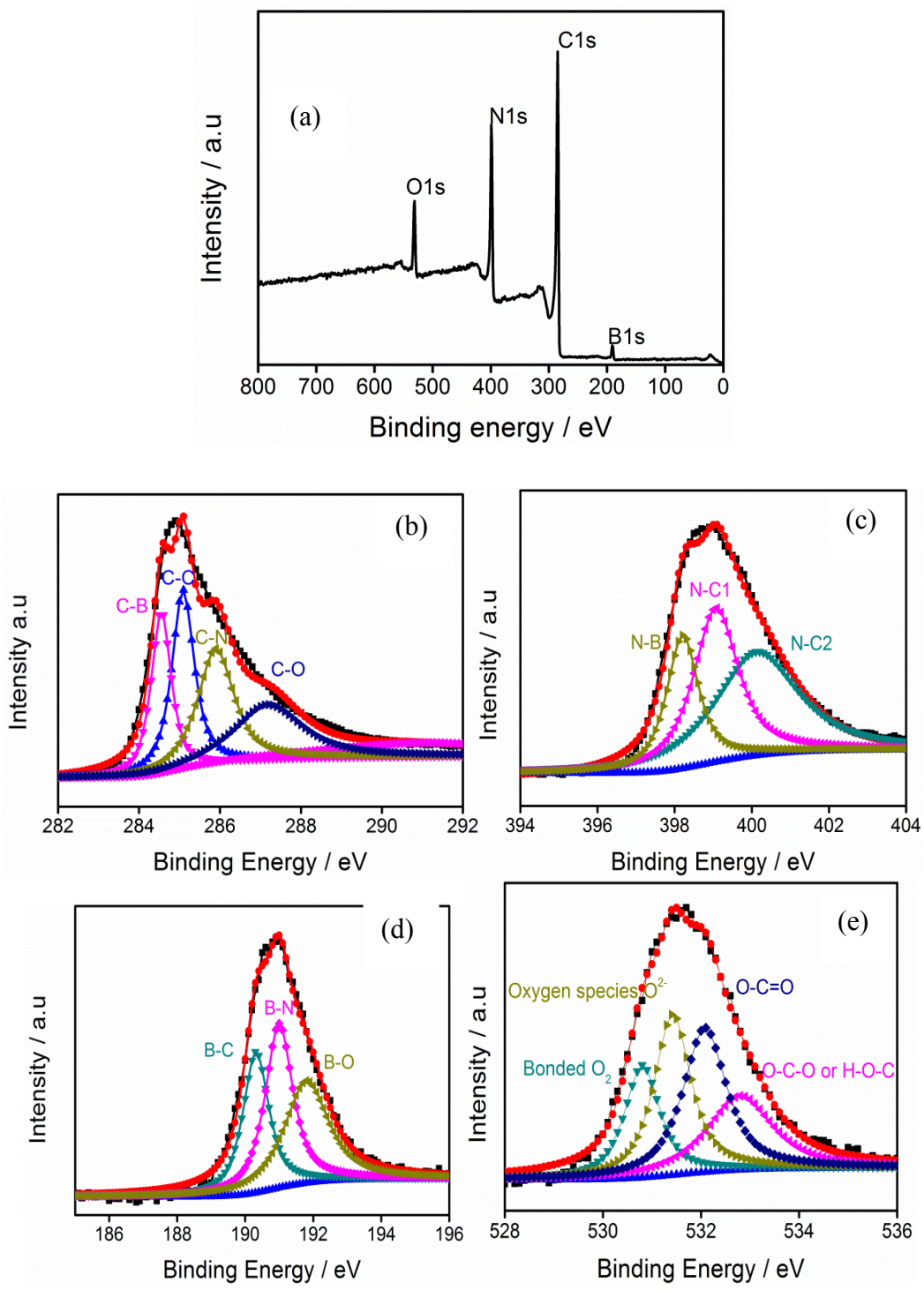

Figure S1. (a) The whole XPS spectra of NBG sample. (b) C1s spectra, (c) N1s spectra, (d) B1s spectra, and (e) O1s spectra of NBG.

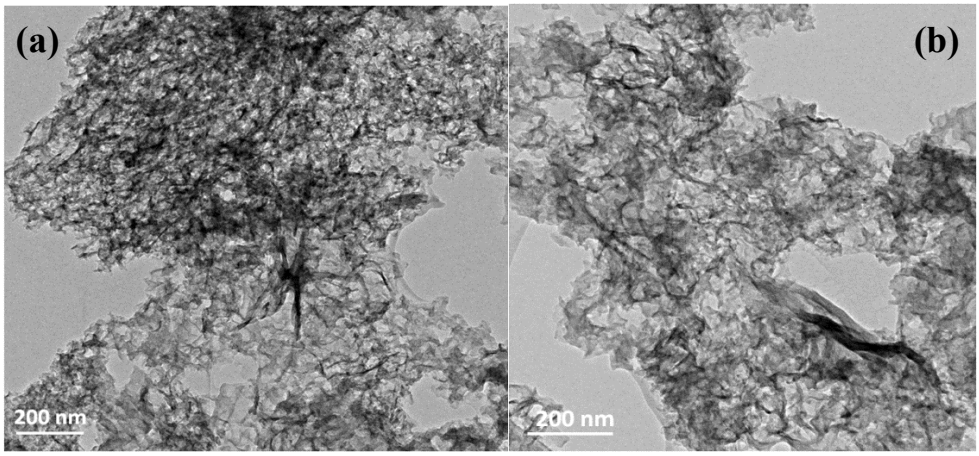

Figure S2. HRTEM images of NBG. Many nanopores can be clearly seen from the NBG planes.

Figure S3. Photo of the NBG colloid solution after 24 h, (2 mg NBG was dispersed in 10 mL water), indicating the colloid is extremely stable.

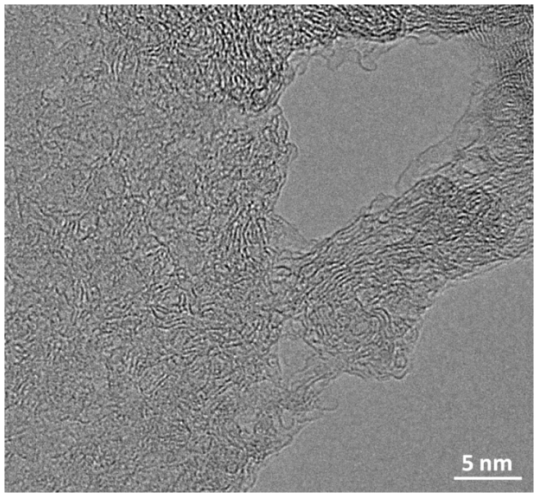

Figure S4. Holes were generated by the irradiation of the electron beam during HRTEM obseravation, indicating the super-thin carbon structure is formed.

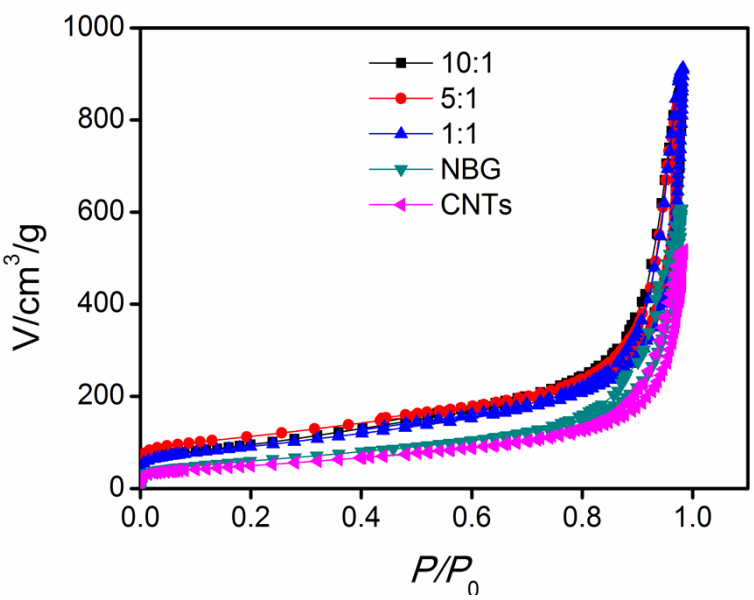

Figure S5. N_2 sorption isotherms of pure NBG, NBG/CNTs (10:1), NBG/CNTs (5:1), NBG/CNTs (1:1), and pure CNTs, respectively.

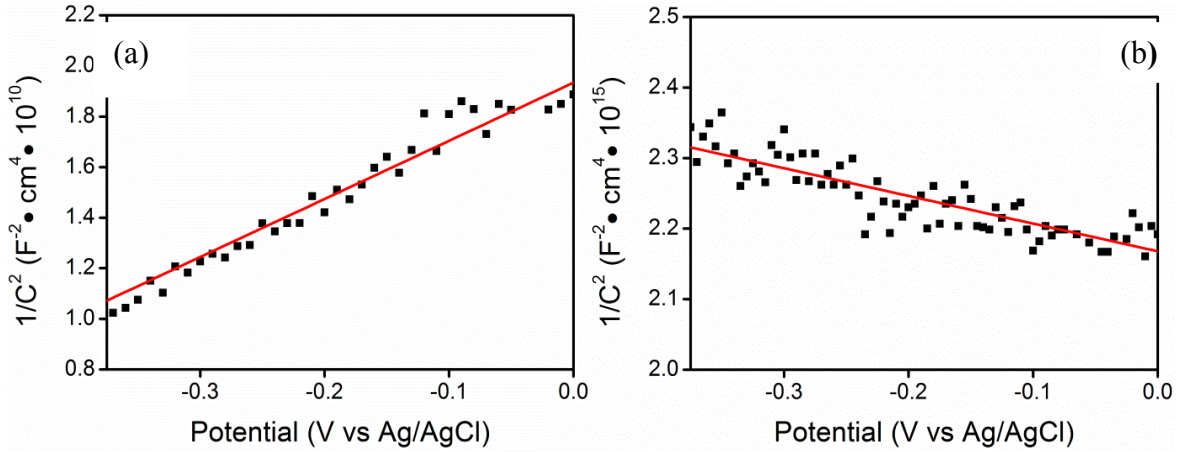

Figure S6. (a) Mott−Schottky plot of the pristine CNTs sample and (b) N, B-codoped graphene sample obtained in 1M NaOH solution using a three-electrode photoelectrochemical cell.

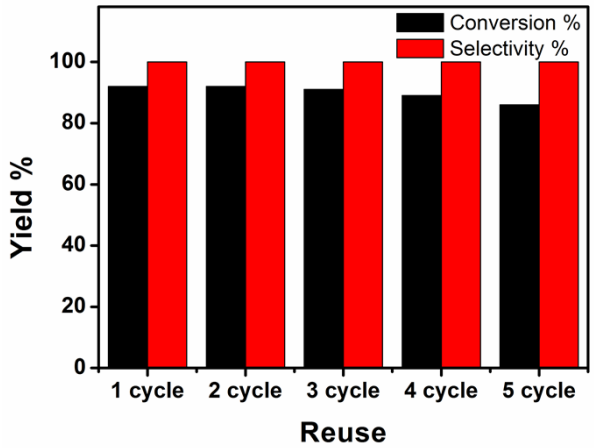

Figure S7. Reusability testing results of the NBG/CNTs (5:1) carboncatalyst. Reaction condition: acetonitrile (5 mL), substrate (1 mmol), catalyst (30 mg), O_2 balloon (1 atm), 3 h, 85°C.

Reference:

[1] X.-H. Li, M. Antonietti, *Angew. Chem. Int. Ed.* **2013**, *52*, 4572.